CLEANUP OF ILMENITE WATER-BASED MUDCAKE

A Dissertation

by

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ABSTRACT

Micronized ilmenite ($FeTiO_3$) was reported as a weighting material in drilling fluids to avoid the disadvantages of barite and to reduce abrasion of wellbore completion. In this dissertation, coreflood tests were applied for the first time to determine the removal efficiency of filter cake generated by water-based drilling fluids based on the micronized ilmenite under high-pressure/high-temperature (HP/HT) conditions. The capacity of different acids to dissolve the micronized ilmenite was also evaluated.

Near-wellbore conditions during the drilling fluid injection and the mudcake cleanup process in sandstone and carbonate cores at reservoir conditions were simulated by coreflood tests. Inductively coupled plasma (ICP), computerized tomography (CT) scans, and scanning electron microscopy (SEM) were used to analyze the solubility of iron and titanium, chemical composition of dried mudcake, and internal structure of the core, respectively.

A complete analysis of the particle size and chemical composition of the ilmenite sample was conducted using Coulter Counter, SEM, and X-ray diffraction (XRD). Several solubility tests were conducted under 200 ℉ to find an optimal solvent to dissolve the micronized ilmenite sample. The solvents include different concentrations of HCl, HEDTA, glycolic acid, formic acid, and a mixture of HCl and HEDTA. An acid solution containing 15 wt% HCl and 8 wt% HEDTA dissolved 98.4 wt% of iron and 76.5 wt% of titanium from the ilmenite sample. It was selected to remove the formation damage and to prevent the iron precipitation in the following coreflood tests.

Coreflood tests were performed under 275 ℉ on Berea and Bandera sandstone core, respectively. 15 wt% HCl had an excellent performance on the dissolution of iron (FeO) and calcium ($CaCO_3$). In Bandera sandstone, 8 wt% HEDTA successfully prevented the iron precipitation. The permeabilities of Berea and Bandera sandstone have increased by 40% and 35.4% after the acid injection, respectively. Outstanding damage removal efficiency from the coreflood study proved that acid solution containing 15 wt% HCl and 8 wt% HEDTA could be served as an efficient solvent for the ilmenite-based drilling fluids.

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CHAPTER I

INTRODUCTION AND LITERATURE REVIEW

Weighting material is a high-density and finely divided solid material used to increase the density of drilling fluids. Nowadays, API standard barite is the most commonly used weighting material (Bruton et al. 2006). However, it has some disadvantages such as sag in drilling fluids and removal difficulty (Ehrhorn and Saasen 1996, Nasr-El-Din et al. 2004). Ilmenite ($FeTiO_3$), which is mainly produced in South Africa, Australia, Canada, and China, has served as a weighting material to avoid the shortcomings of barite (Al-Bagoury and Steele 2012; Xiao et al. 2013). Features of ilmenite and API standard barite (Bruton et al. 2006, Amighi and Shahbazi 2010) are compared in Table 1.

Table 1 Properties of Weighting Materials

	API Standard Barite	Regular Ilmenite
Main Component	$BaSO_4$	$FeTiO_3$
Average Particle Size, μm	15-20	30-45
Density, g/cm^3	4.2-4.5	4.5-5.1
Mohs Scale of Hardness	3-3.5	5-6

The rate of penetration (ROP) in shale was enhanced by replacing barite with ilmenite in water-based drilling fluids (Blattel and Rupert 1982). Besides the enhancement of the rheological and filtration properties, using ilmenite as a weighting agent could also improve the performance of drilling fluids in the facets of occupational hygiene and reutilization (Fjogstad et al. 2000).

Acid solubility of ilmenite is of great significance to remediate any change that might occur during its use in the drilling operations. The chemical reactions of ilmenite dissolution in hydrochloric acid can be defined as (Jonglertjunya and Rubcumintara 2013):

$$HCl + H_2O \rightarrow H_3O^+ + Cl^- \quad \text{-------------------- (1)}$$

$$FeTiO_3 + 4H_3O^+ \rightarrow Fe^{2+} + TiO^{2+} + 6H_2O \quad \text{-------------------- (2)}$$

The main control factors of the rate of these reactions are particle size, acid concentration, temperature, stirring, additives, and acid-to-ilmenite mole ratio (van Dyk et al. 2002). The high concentration of HCl is an effective dissolvent to ilmenite under laboratory circumstance, but it is highly corrosive to wellbore tubulars at high temperature.

Because of a host of problems caused by the use of HCl both in carbonates and sandstones at high temperature, adding organic acid to HCl is more helpful than using either single acid, such as maximum corrosion inhibition and enhancement of acid penetration (Dill and Keeney 1978, Chang et al. 2008). Chelating agents are considered to be another type of complex organic acid used in the oilfield (Al-Harthy et al. 2008). They provide advantages on well stimulation at high temperatures, such as retarded reaction rates, low corrosion rates and improved health, safety, and environmental benefits.

Although ilmenite generally performed positively for the application in drilling fluids, the high specific gravity and hardness of ilmenite could give rise to an increasing abrasion in fluid systems (Fjogstad et al. 2000, Saasen et al. 2001). Field works showed in the circulation system, the normal size ilmenite performed a higher flow-induced abrasion in high-velocity parts than barite (Blomberg et al. 1984). Because of the high specific gravities, the coarse grade of ilmenite showed high dynamic and static sag (Tehrani et al. 2014).

To achieve a finer size grade and to reduce the abrasion, Al-Bagoury and Steele (2012) reported the use of micronized ilmenite with an average particle size (D_{50}) of 5 μm as a weighting material. Under similar conditions, the micronized ilmenite showed low sag tendency and low plastic viscosity compared to API barite. These desirable features can be applied in challenging drilling operations such as horizontal drilling, deep water, and slimehole. Elkatatny et al. (2012) reported a complete evaluation of the ilmenite-based drilling fluids and its filter cake in HP/HT conditions. A minimal amount of $CaCO_3$ solids could decreased the filtrate volume because of its benefit in particle packing. After a 16 hours soaking by the filtration loss equipment, the ilmenite-based filter cake was removed completely after the reaction with 5 wt% HCl (Elkatatny et al. 2013).

The principal objective of this dissertation is to apply coreflood tests for the first time to remove the filter cake caused by water-based drilling fluids containing micronized ilmenite. Firstly, an average particle size and chemical composition of ilmenite sample were determined. Then, several solubility tests were conducted to evaluate the capacity of different solvents to dissolve micronized ilmenite. Finally, near-wellbore conditions during the drilling fluid injection and the mudcake cleanup process in sandstone and carbonate cores at reservoir conditions were simulated by coreflood tests. The removal efficiency of formation damage was determined by the permeability changes.

CHAPTER II

EXPERIMENTAL STUDIES

2.1 Materials

Micronized ilmenite was used as weighting material to prepare the water-based drilling fluids.

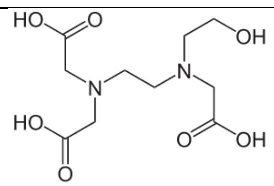
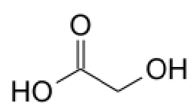
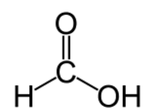
Solutions of 5, 10 and 15 wt% of HCl, 20 wt% HEDTA, 9 wt% formic acid, 10 wt% glycolic acid, and an acid solution containing 15 wt% HCl and 8 wt% HEDTA were used in solubility tests (Table 2).

Table 2 Acid Solutions for Solubility Tests

	Concentration	pH
HCl	5%	< 0
	10%	< 0
	15%	< 0
HEDTA	20%	4
Glycolic Acid	10%	1.9
Formic Acid	9%	1.7
HCl + HEDTA	15% + 8%	0.4

HCl does not react easily with minerals that reduce sandstone permeabilities. However, HCl reacts with carbonate reservoirs, especially limestone and dolomite to form wormholes (Al-Harthy et al. 2008). HEDTA, glycolic acid, and formic acid (Table 3) are organic acids with low corrosivity.

Table 3 Properties of Organic Acids

	HEDTA	Glycolic Acid	Formic Acid
Systematic Name	N-hydroxyethyl-ethylenediamine-triacetic acid	2-hydroxyethanoic acid	Methanoic acid
Structural Formula			
Features	• Chelating Agent • Low corrosivity • Only chelate with divalent and trivalent cations	• Low corrosivity • Low toxicity • Excellent solubility in hard waters	• Used as corrosion inhibitor intensifier at high temperature

HEDTA is a chelating agent, which can only chelate with divalent and trivalent cations. It is particularly effective for preventing iron precipitation at a high pH. Glycolic acid is the smallest α-hydroxy acid, which has a low molecular weight and dual functionality of alcohol and acid. As an intensifier, formic acid is more suitable for high temperature circumstance (Dill and Keeney 1978, Chang et al. 2008).

The drilling fluid was prepared according to the formula in Table 4 (Elkatatny et al. 2012).

Table 4 Formula of Water-Based Drilling Fluid (Elkatatny et al. 2012)

Additive	Function	Lab Unit, g	Mixing Time, min
Deionized Water	Base Fluid	290	-
Defoamer	Anti-Foaming Agent	0.08	1
Xanthan Gum	Viscosifier	0.25	20
Modified Starch	Fluid Loss Control Agent	5	20
Polyanionic Cellulose Regular Grade	HP/HT Filtrate Control Agent	1	20
Potassium Chloride	Density and Shale Inhibitor	72	20
Potassium Hydroxide	pH Control Agent	1	1

Table 4 Continued

Additive	Function	Lab Unit, g	Mixing Time, min
Calcium Carbonate Fine (25 µm)	Bridging Material	7	20
Calcium Carbonate Medium (50 µm)		3.5	
Micronized Ilmenite	Weighting Material	300	20

A certain amount of defoamer, deionized water, xanthan gum, modified starch, polyanionic cellulose regular grade, potassium chloride, potassium hydroxide, a mixture of 7 g of 25-µm and 3.5 g of 50-µm $CaCO_3$, and micronized ilmenite were mixed chronologially. Table 5 shows the density and the rheological properties of the drilling fluid.

Table 5 Properties of Drilling Fluid

Property	Temperature, °F	Value	Unit
Density	77	110	pcf
pH	77	9	–
Plastic Viscosity	120	32	cp

Table 5 Continued

Property	Temperature, ℉	Value	Unit
Yield Point	120	24	lb/100 ft^2
10 s Gel Strength	120	3	lb/100 ft^2
10 min Gel Strength	120	5	lb/100 ft^2

In coreflood tests, two kinds of sandstone cores, Berea and Bandera, were applied. The dimensions of the cores are 6 in. length and 1.5 in. diameter. The pore volumes of the two sandstone cores were found to be 31.20 and 28.29 cm^3, respectively. The mineralogy of Berea and Bandera are given in Table 6.

Table 6 Mineral Composition (Mahmoud et al. 2011)

Mineral, wt%	Berea	Bandera
Quartz	86	57
Dolomite	1	16
Calcite	2	-
Feldspar	3	12
Kaolinite	5	3
Illite	1	10
Chlorite	2	1

2.2 Equipment

Solubility tests were performed in a batch reactor under magnetic stirring, which is illustrated in Figure 1 (Al Moajil and Nasr-El-Din 2010).

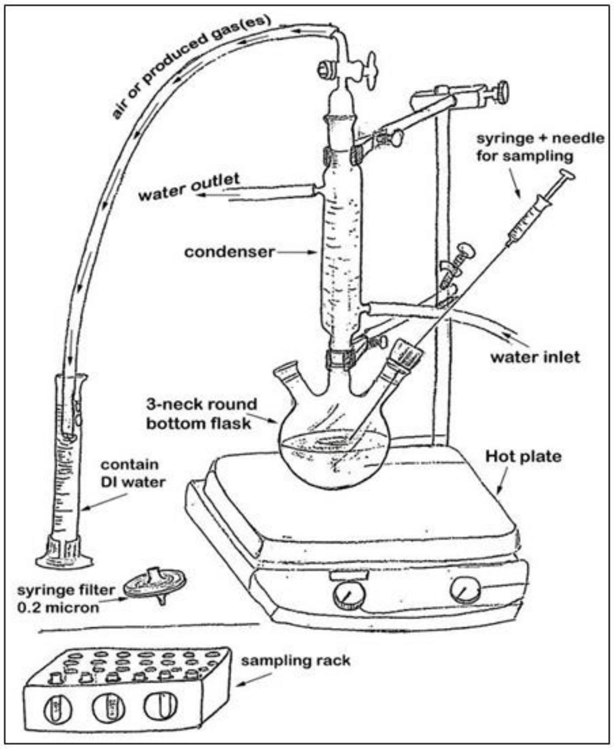


Figure 1. Solubility setup (Al Moajil and Nasr-El-Din 2010).

Both a scanning electron microscopy (SEM) and X-ray diffraction (XRD) were used to assess the chemical composition of a provided ilmenite sample. Surface and chemical analysis as well as imaging of the sample was obtained by the SEM. XRD provides detailed information on the spectrum and physical properties of the sample.

The particle size distribution was reported as equivalent spherical diameters using Multisizer 3 Coulter Counter. The particles were suspended in a methanol chloride electrolyte solution. The particles in the solution passed through a 100 µm aperture tube concurrent with an electrical current. As the particles passed through the tube, an electrical "spike" was generated, which is directly proportional to the particle's volume.

The inductively coupled plasma (ICP) instrument was utilized to obtain the iron and titanium concentrations from the diluted liquid samples. A Eutech 700 pH meter was utilized to the test the pH value.

Coreflood tests (Figure 2) were used to obtain the permeability of the core and assess the formation damage removal, and the Universal HD-350E X-ray CT scanner with a 0.35 mm spatial resolution (0.25 mm on enhanced) was used to obtain the internal structure of the cores.

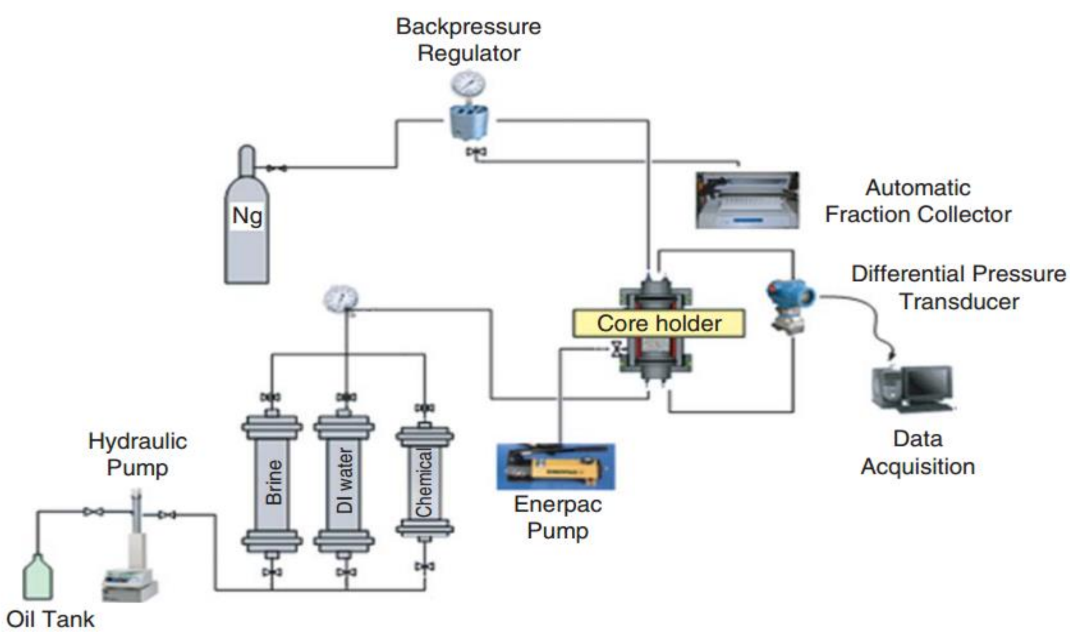


Figure 2. Coreflood setup (El-Monier and Nasr-El-Din 2013).

2.3 Procedures and Parameters

Because ilmenite-based drilling fluids tend to form filter cake, the solubility of ilmenite in different acids needs to be tested to ensure a certain acid solution can dissolve ilmenite under reservoir temperature. A 10-hour solubility test procedure included:

1) A 250 cm^3 acid solution was added into a batch reactor. The temperature was set to 200 ℉ under atmospheric conditions.

2) A 4 g of ilmenite sample was added when the solution reached 200 ℉. Magnetic stirring was started simultaneously.

3) The 3-5 cm^3 liquid samples were collected using a syringe and filtered by a 0.2-µm Whatman syringe filter immediately. Sampling frequency was once every 15 minutes during the first hour of the experiment and once per hour for a period of 10 hours.

In a coreflood test, the back pressure and overburden pressure were set at 1100 psi and 2000 psi, respectively. The procedure of the coreflood tests was as follows:

1) The initial permeability of the core was measured using brine (5 wt% KCl) under room temperature.

2) The drilling fluid was injected into the core at 275 ℉.

3) The filter cake was removed from the inlet surface (Figure 3) and collected.

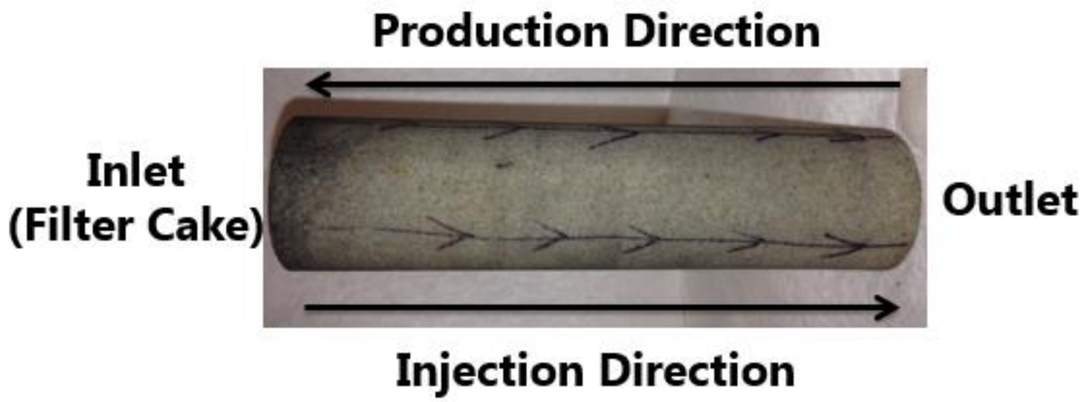


Figure 3. The original Berea sandstone core after the external filter cake was removed.

4) The damaged permeability was measured using brine at room temperature in the production direction.

5) To remove the damage, 6 pore volumes of the acid solution containing corrosion inhibitor, intensifier, and 5 wt% KCl was injected by 5 cm^3/min at 275 ℉. Effluent samples were taken from the core every two minutes during a one-hour test.

6) The final permeability was measured using brine at room temperature in the production direction.

The core at three different steps (Figure 4) were used to evaluate the damage removal: the original core, the core after the filter cake was formed, and the core after the external filter cake was removed. Using the pressure drops recorded at these three steps, the initial, damaged, and final permeabilities were calculated using Darcy’s Law.

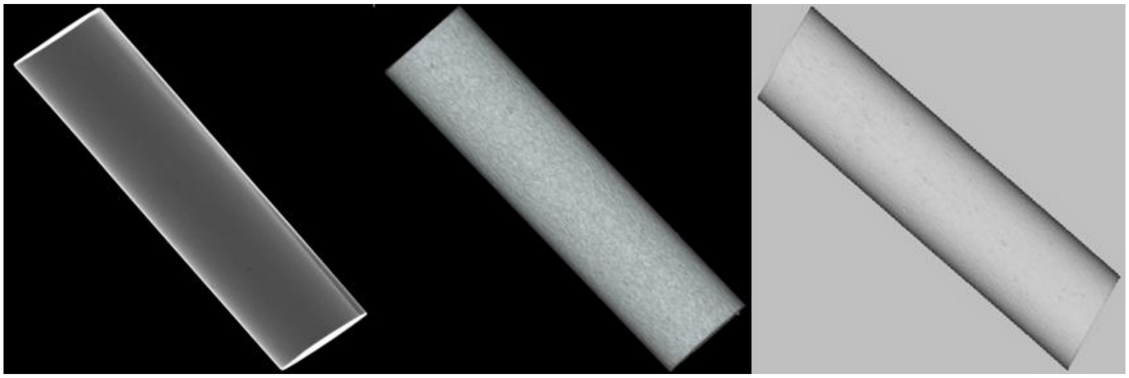


Figure 4. CT scan images of the original Berea sandstone core, the core after the filter cake was formed, and the core after the external filter cake was removed (from left to right).

CHAPTER III

RESULTS AND DISCUSSION

3.1 Particle Sizing

The particle size distribution of the micronized ilmenite sample was tested five times by Coulter Counter. The average equivalent spherical diameter is 3.839 μm (Table 7).

Table 7 Particle Size of Micronized Ilmenite

Test Number	Equivalent Spherical Diameter, μm
1	3.901
2	3.842
3	3.775
4	3.719
5	4.174
Average	3.839

Based on the particle size distribution (Figure 5), the micronized ilmenite are able to have a positive effect on rheology properties with potential benefits to drilling hydraulics and rate of penetration (Tehrani et al. 2014).

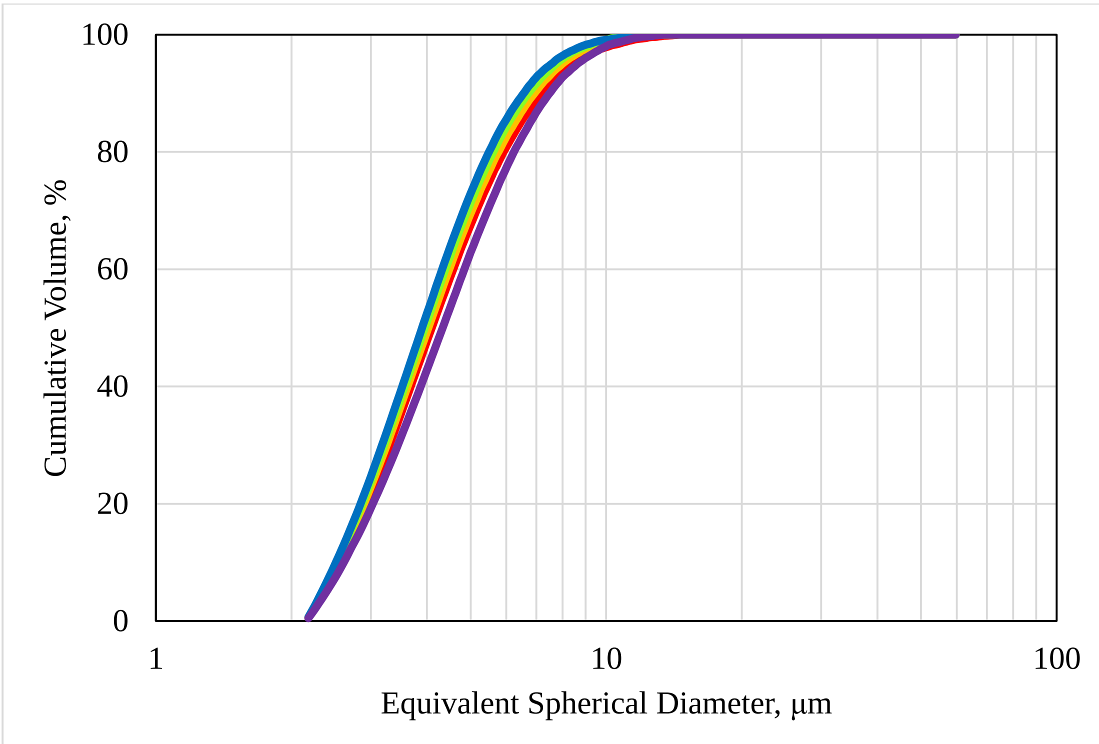


Figure 5. Particle size distribution of micronized ilmenite sample.

3.2 Chemical Analysis of Ilmenite

The EDX spectrum of the micronized ilmenite sample as received is presented in Figure 6.

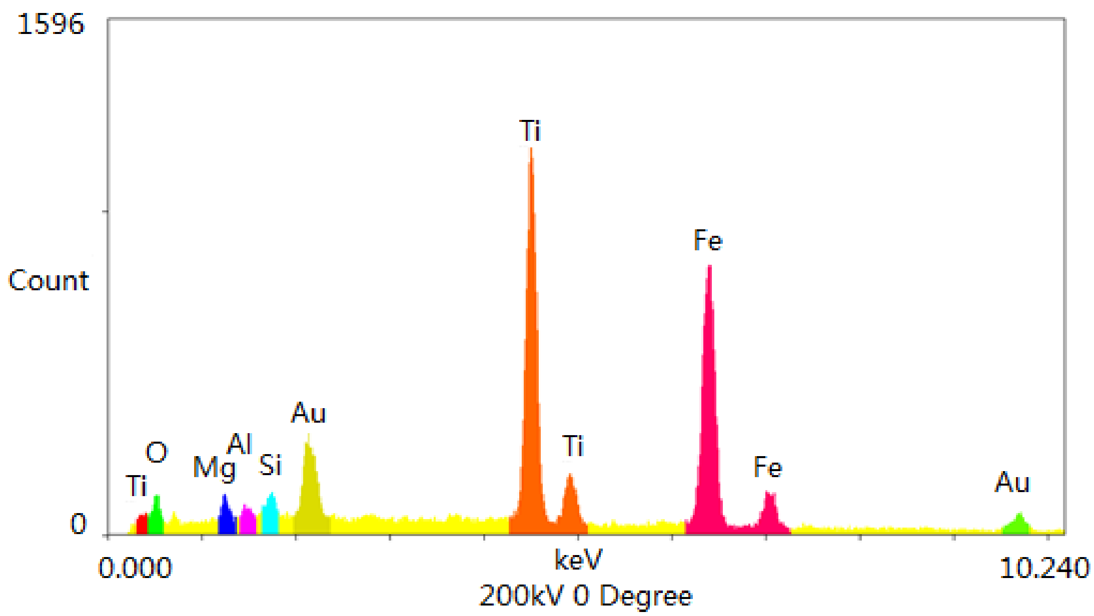


Figure 6. EDX spectrum of ilmenite sample as received.

Compared with the yellow scale in Figure 7, the SEM photo showed that the average size of the ilmenite is narrower than 5 μm.

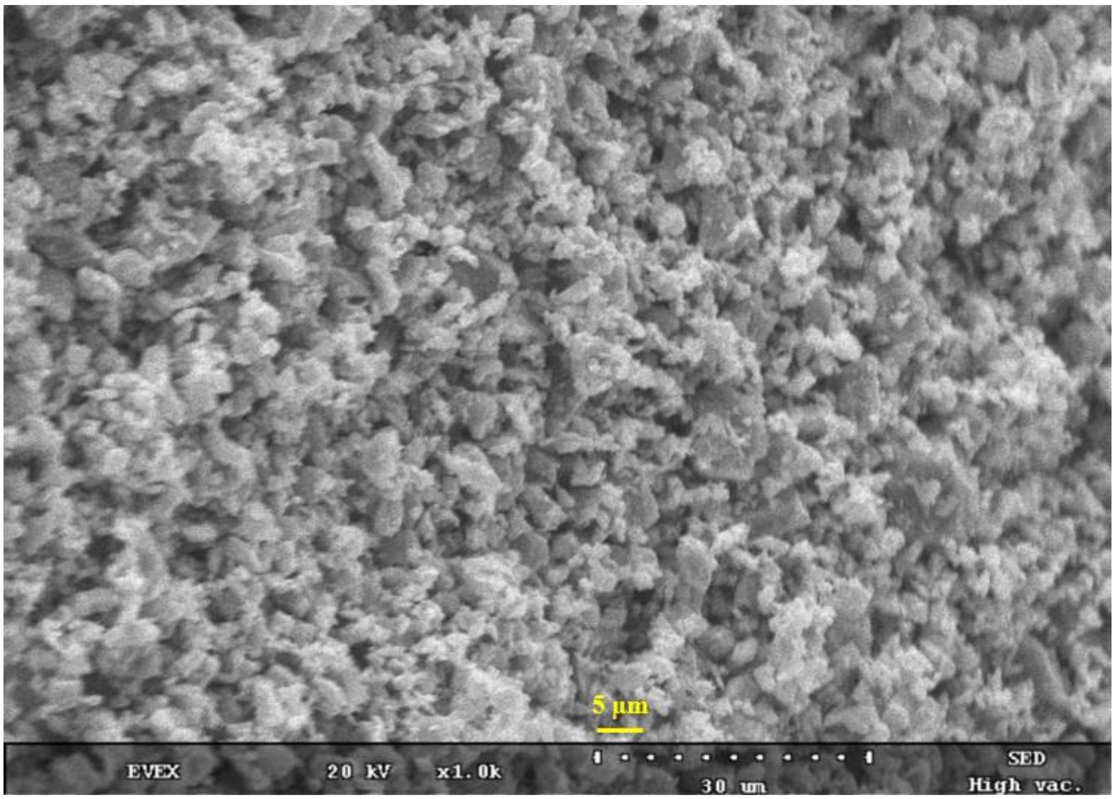


Figure 7. SEM photo (1 kX) of the surface of the ilmenite sample.

The weight percentage of each of the oxides in the sample is shown in Table 8. As the main components of ilmenite ($FeTiO_3$), FeO and TiO_2 presented 41.22 wt% and 47.13 wt%, respectively.

Table 8 Chemical Composition of Ilmenite

Oxides	Concentration, wt%
TiO_2	47.13
FeO	41.22
MgO	5.68
SiO_2	3.86
Al_2O_3	2.11

In Figure 8, a XRD spectrum of the ilmenite sample is presented. The powder XRD pattern for the sample (black line) is well matched by the pattern of $Fe^{2+}TiO_3$ (red lines) provided by the database of XRD system.

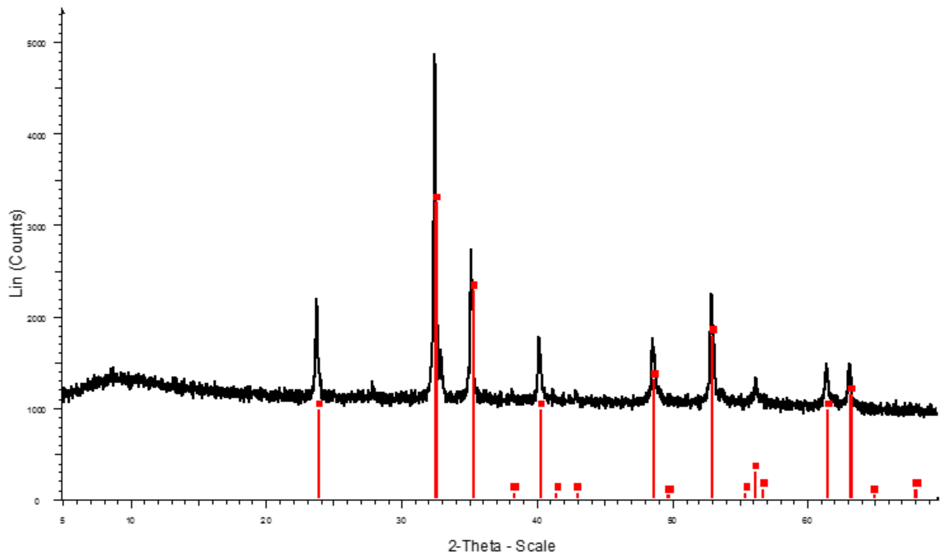


Figure 8. X-ray diffraction spectrum of ilmenite sample. Black and red lines represent the powder XRD pattern for the sample and the pattern from the database of $Fe^{2+}TiO_3$, respectively.

3.3 Solubility Test

The weight of iron and titanium in 4 g of ilmenite samples were calculated from the chemical composition analysis. The weight of iron and titanium dissolved in different solvents was calculated from ICP results of the diluted liquid samples. The dissolved weight percentage of iron and titanium in different time steps was obtained by dividing the latter by the former. The dissolving rates of iron and titanium were also calculated from the concentrations. The results are plotted in Figures 9 to 11, and the dissolved percentages after 15 minutes and 10 hours are shown in Table 9.

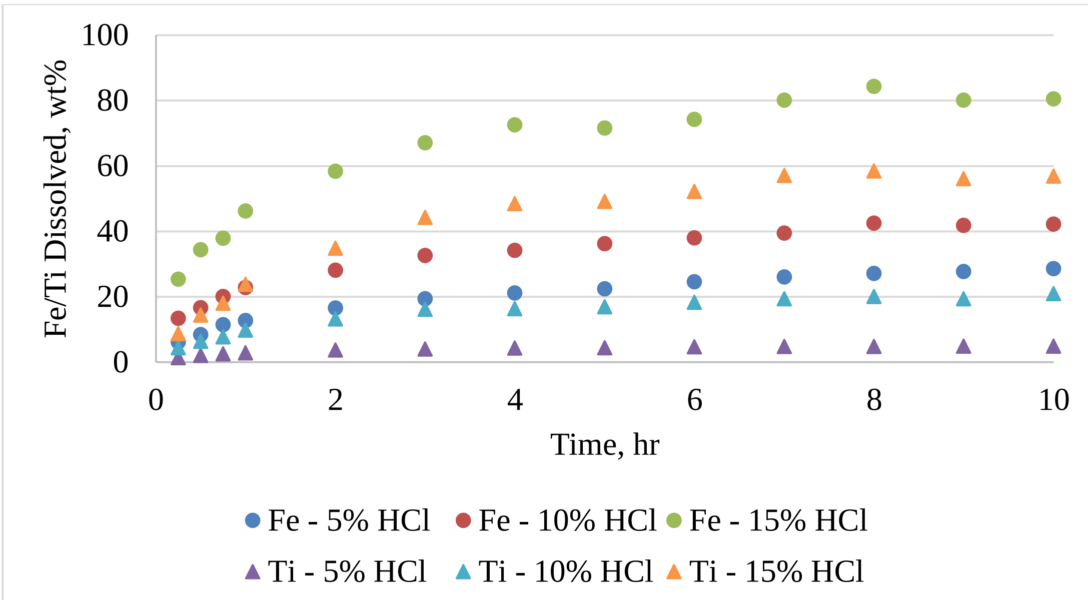


Figure 9. Iron and Titanium dissolution of the ilmenite sample in different HCl concentrations.

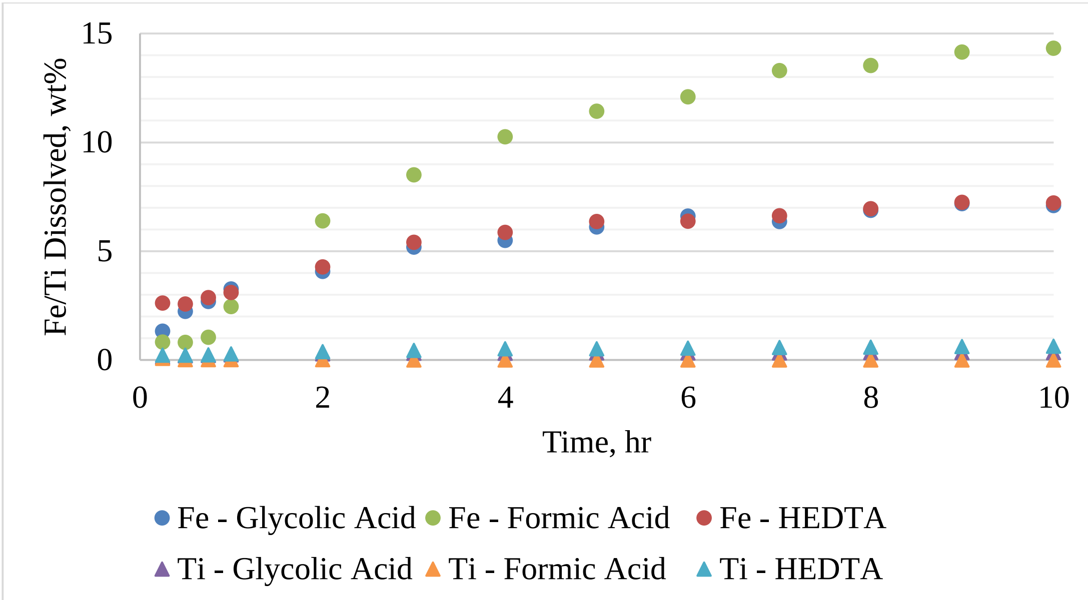


Figure 10. Iron and Titanium dissolution of the ilmenite sample in organic acids.

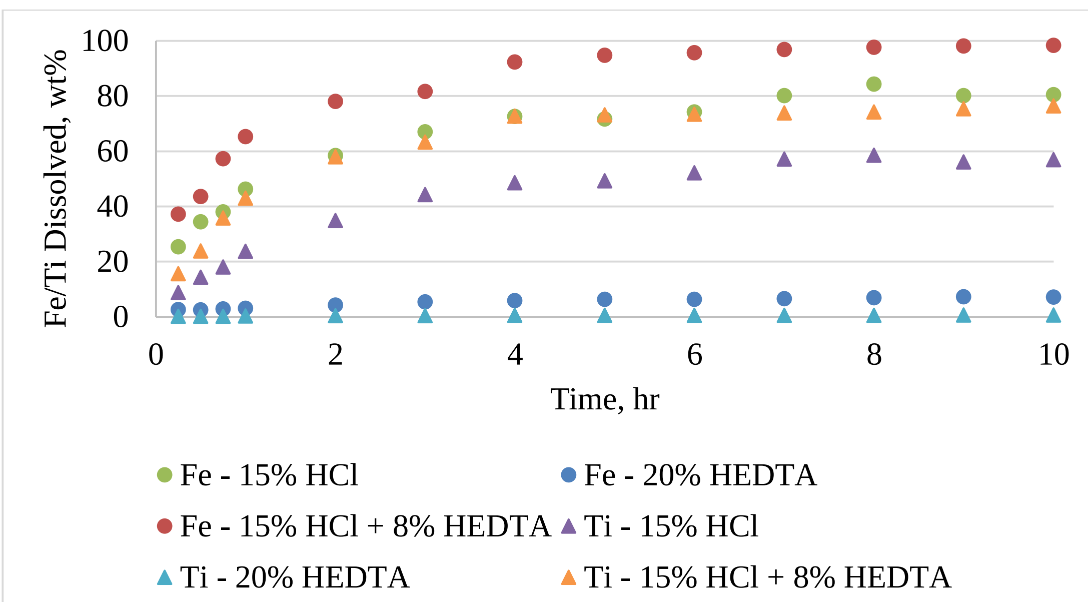


Figure 11. Iron and Titanium dissolution of the ilmenite sample in HCl and HEDTA.

Table 9 Iron and Titanium Dissolved after 10-Hour Solubility Tests

Solvent	Fe Dissolved, wt%	Ti Dissolved, wt%
5 wt% HCl	28.7	5.0
10 wt% HCl	42.2	21.0
15 wt% HCl	80.5	56.9
HEDTA	7.2	0.64
Glycolic Acid	7.1	0.35
Formic Acid	14.3	0
HCl + HEDTA	98.4	76.5

According to the results, with the increase of the concentration of HCl from 5 to 15 wt%, the dissolving efficiency of iron and titanium increased significantly. The ilmenite sample obviously dissolved more in HCl than in the three organic acids which showed extremely low solubilities of titanium. These organic acids are not able to dissolve ilmenite individually. Especially, the tetravalent titanium in ilmenite cannot be dissolved by HEDTA which can only chelate with divalent and trivalent cations.

Interestingly, the acid solution containing 15 wt% HCl and 8 wt% HEDTA significantly dissolved more of the ilmenite sample than 15 wt% HCl. As introduced above, adding organic acid into HCl can enhance the acid penetration (Chang et al. 2008). Due to the low dissociation constant, HEDTA did not dissociate to generate hydrogen ions when it mixed with HCl. Until the hydrogen ions from HCl have been used out, the carboxylic groups of HEDTA stopped preserving and started to dissociate, leading to a promoted dissolution of ilmenite. After the 10-hour solubility test, the acid solution, which dissolved 98.4 wt% of iron and 76.5 wt% of titanium from the ilmenite sample, showed strong solubility and dissolving efficiency which proved that adding HEDTA to 15 wt% HCl can enhance the dissolution of ilmenite.

3.4 Coreflood Test

The EDX results of the dried mudcake from the coreflood test using a Berea sandstone core are presented in Figures 12 and 13 as well as Table 10.

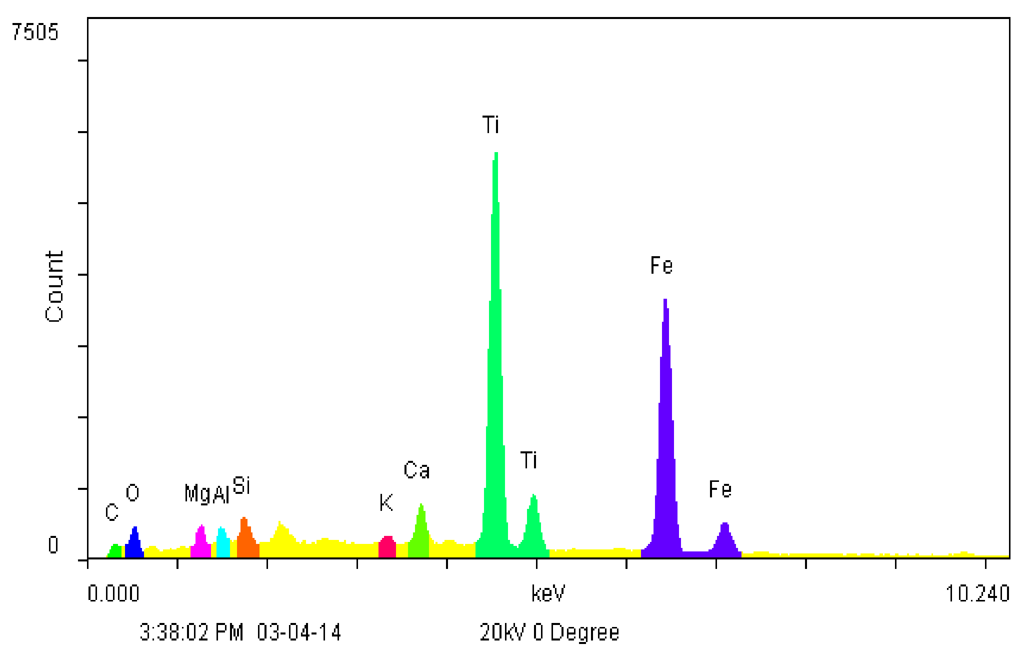


Figure 12. EDX spectrum of mudcake from the coreflood test using a Berea sandstone core.

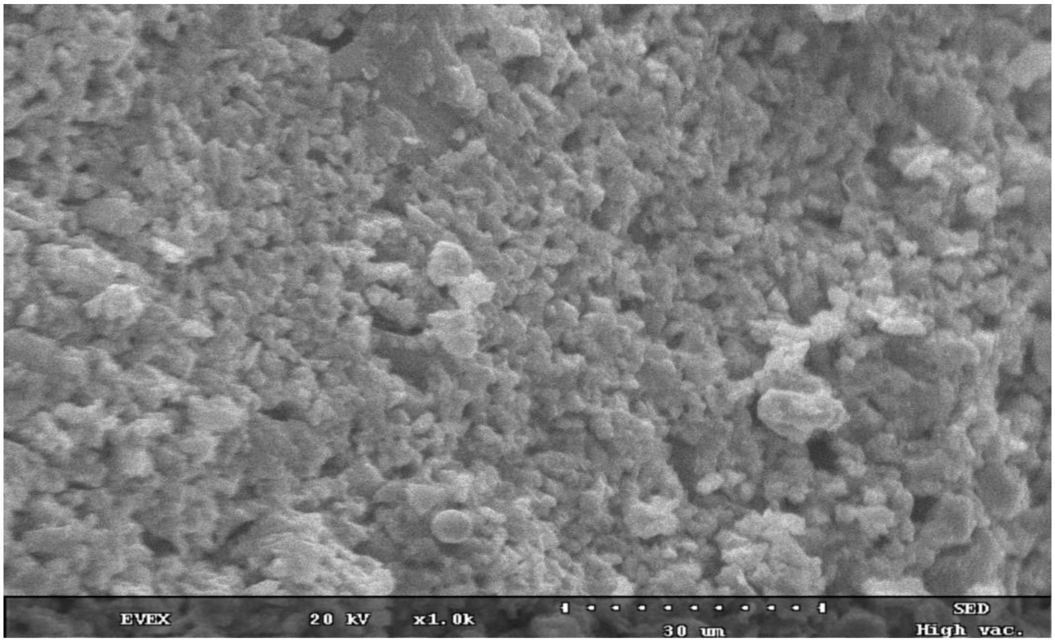
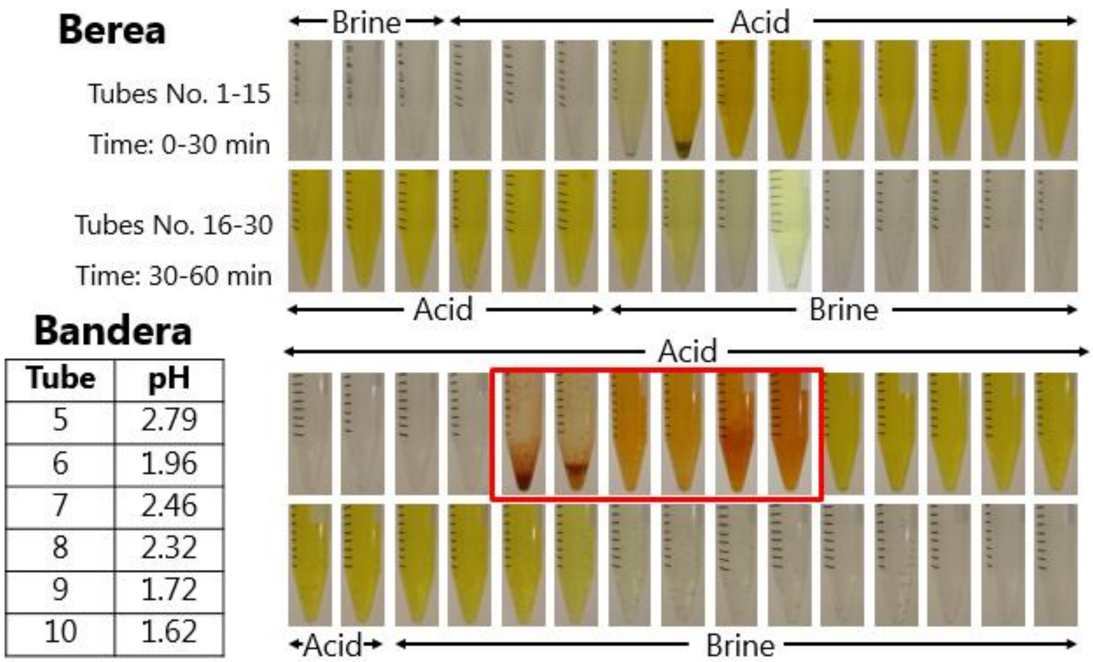


Figure 13. SEM photo (1 kX) of the surface of mudcake from the coreflood test using a Berea sandstone core.

Table 10 EDX Results of Coreflood Mudcake

Element	Concentration, wt%
Fe	46.10
Ti	38.53
Ca	5.16
Mg	3.45
Al	3.08
Si	3.03
K	0.64

The samples collected during the tests using 15 wt% HCl are shown chronologically in Figure 14.



Tube	pH
5	2.79
6	1.96
7	2.46
8	2.32
9	1.72
10	1.62

Figure 14. Samples collected from the coreflood tests using 15 wt% HCl.

In the coreflood test, using the Bandera sandstone core, some tubes (marked in the red rectangle) contained brownish-red flocculent precipitate $Fe(OH)_3$. The pH values of these tubes were measured to be approximately in the range of 2 to 3. To prevent this iron precipitation, the acid solution containing 15 wt% HCl and 8 wt% HEDTA was used to substitute the conventional HCl system. The samples collected during the tests using the acid solution are shown chronologically in Figure 15. At a similar pH range and iron concentration, no iron precipitation was observed, which indicates that adding 8 wt% HEDTA successfully stabilized the iron ions in Bandera sandstone.

Bandera

Tube	pH
5	7.18
6	3.28
7	2.78
8	2.41
9	2.26
10	1.55

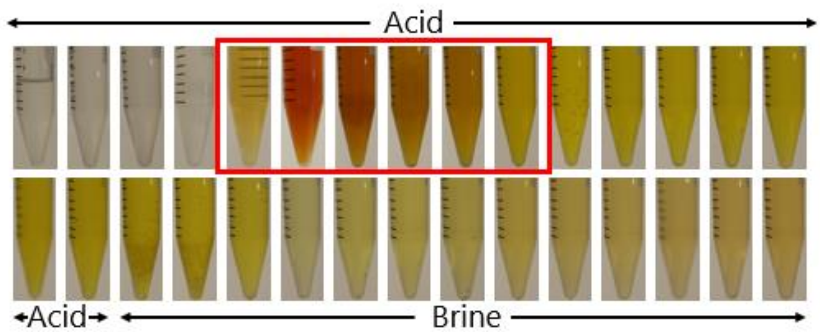


Figure 15. Samples collected from the coreflood tests in Bandera sandstone using the acid mixture.

The concentrations of iron, titanium, calcium, magnesium, and aluminum tested from the samples collected from the coreflood tests using Berea and Bandera sandstone cores are plotted in Figures 16 and 17.

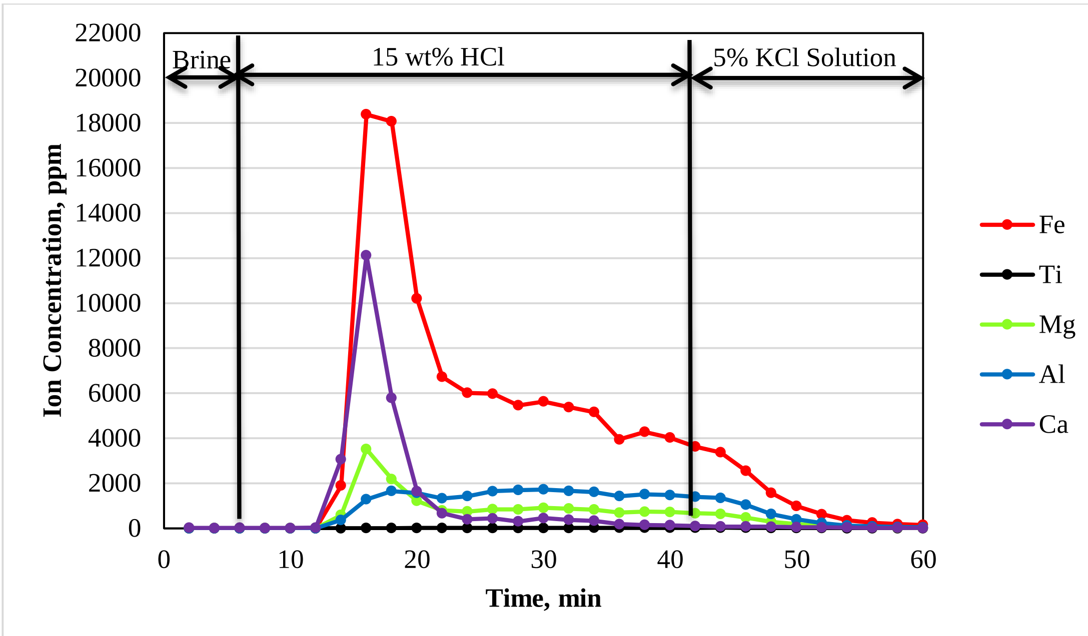


Figure 16. Ion concentration in samples collected from coreflood test under 275 ℉ using a Berea sandstone core.

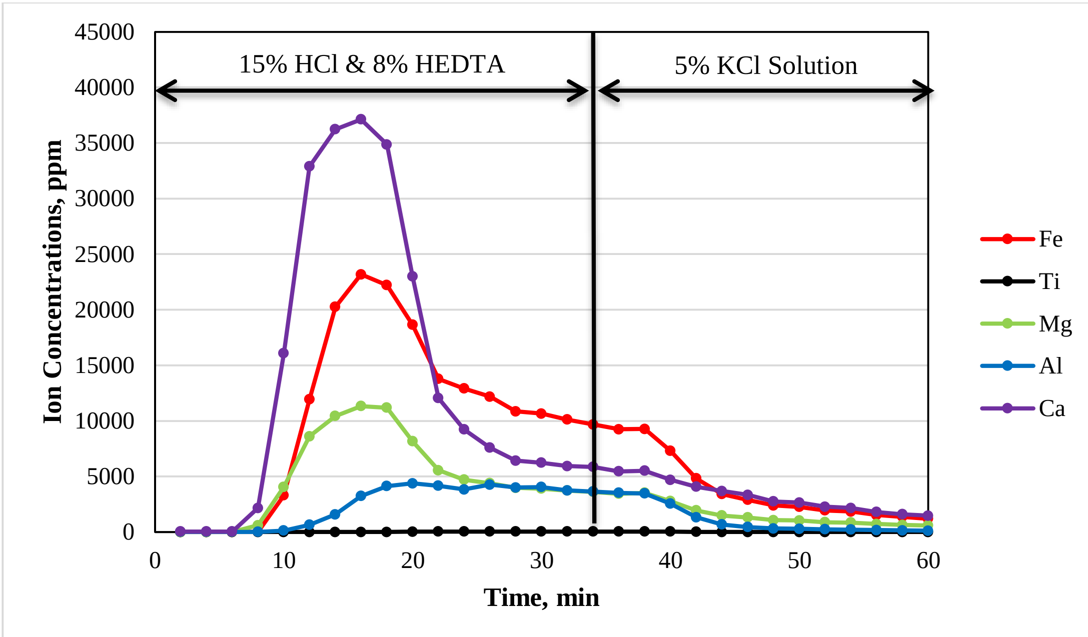


Figure 17. Ion concentration in samples collected from the Bandera coreflood test under 275 ℉ using the acid solution.

Samples from the test using the Bandera sandstone core have significantly higher calcium concentrations than the one using the Berea sandstone core. According to **Table 6**, the Bandera sandstone core contains 12 wt% Ca-feldspar and 16 wt% dolomite which are major sources of calcium.

Depending on the results, 15 wt% HCl had an excellent performance on the dissolution of iron oxides and calcite ($CaCO_3$). However, compared to the significant dissolution of titanium oxide in the solubility test, titanium oxide was hardly dissolved in the coreflood test. The probable reason of this significant difference is that iron and titanium react with the acid separately. Based on van Dyk et al. (2002), the reaction between titanium (TiO_2) and hydrochloric is complex because the reaction rate is controlled by the time-varying titanium species in solution. Also, any additives, including other components in the drilling fluids will influence the formation of titanium species. The relatively high solubility of titanium needs to take place in a closed system and enough reaction time, but the coreflood test does not provide these. The 10-hour solubility test was conducted in a flask which could be considered a closed system, but the coreflood test was conducted in an open system. The flowing acid in the coreflood test resulted in an insufficient reaction time between the acid and the mudcake, which exaggerated the dissolution of titanium.

The initial, damaged, and final permeabilities were calculated using Darcy's Law. Retained permeability, which is used to evaluate the removal efficiency of formation damage, was calculated by following equation using the initial and final permeabilities:

$$k_{retained} = \frac{k_{final}}{k_{initial}} \times 100\% \qquad \text{--------------------} \ (3)$$

The comparison between different permeabilities is summarized in Figure 18. Damaged permeability decreased after the mud injection. Compared to the initial permeability, the final permeability had increased after 15 wt% HCl injection. Retained permeabilities of the Berea and Bandera sandstone core are 140% and 114.5%, respectively. After injected the acid solution containing 15 wt% HCl and 8 wt% HEDTA, the retained permeability of Bandera sandstone core is 135.4%. Outstanding damage removal efficiency from the coreflood study proved that the 15 wt% HCl solution cooperated with HEDTA could be served as an efficient solvent for the ilmenite-based drilling fluids.

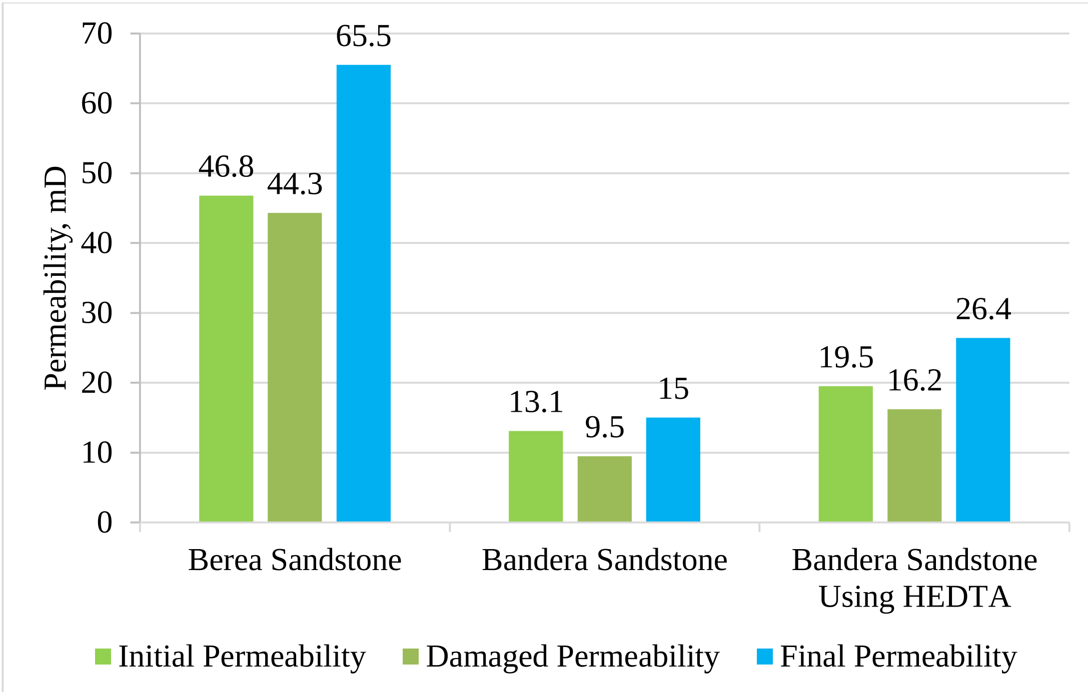


Figure 18. Comparison between different permeabilities.

CHAPTER IV

CONCLUSIONS

1. Coreflood tests were performed for the first time to remove the mudcake caused by water-based muds containing micronized ilmenite.

2. A solution of 20 wt% HEDTA, 10 wt% glycolic acid, and 9 wt% formic acid at lower pH is not able to dissolve ilmenite individually due to the low solubility. However, the dissolution was enhanced significantly by adding HEDTA into HCl. After the 10-hour solubility test, the acid solution containing 15 wt% HCl and 8 wt% HEDTA dissolved 98.4 wt% of iron and 76.5 wt% of titanium.

3. In the coreflood tests, the permeabilities of Berea and Bandera sandstone have increased by 40% and 35.4%, respectively, after the acid injection. Due to the strong solubility and dissolving efficiency, the acid solution containing 15 wt% HCl and 8 wt% HEDTA could be served as an efficient solvent for the ilmenite-based drilling fluids.

4. Added to the 15 wt% HCl solution, 8 wt% HEDTA successfully stabilized the iron ions in Bandera sandstone.

5. HCl had a strong performance on the dissolution of iron. On the other hand, titanium could not be dissolved. A closed system and sufficient reaction time are required to enhance the dissolving efficiency of titanium in a coreflood test.

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